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(54) **METHOD FOR TREATING LIQUID WASTE FROM A NUCLEAR POWER PLANT WITH BORON CONTROL**

(57) The invention relates to the complex processing of NPP's liquid, boron-containing waste with a complex composition, being generated during the operation of nuclear power plants, including of ones VVER-type, and can be used to isolate boric and nitric acids and hydroxides of sodium and potassium for their reuse in the NPP process cycle. They execute introduction of calcium nitrate at pH 9.3-11.0 into the initial borate solution, comprising nitrates and sodium and potassium sulphates, with obtaining a co-precipitation of calcium borate and sulphate, which they separate from the mother liquor. Then they treat co-precipitation of calcium borate and sulphate with a nitric acid solution until pH 5-7 is provided and at transforming of calcium borate into the solution and separation of the calcium sulphate sediment. They treat calcium borate solution with nitric acid at a temperature of 10-20°C until pH 1-3 is provided and with formation of the boric acid sediment, which they separate from the calcium nitrate solution, wash with a nitrate solution

of pH 2-3, comprising 30-35 g/l of boric acid, and dry at a temperature not exceeding 60°C. After separation of boric acid sediment they add calcium nitrate solution to the initial borate solution. They subject mother liquor to electrodialysis in a three-chamber electrodialysis device with cation-exchange and anion-exchange membranes at a current value of 1-3 A and a voltage of 4-10 V. They conduct electrodialysis at the ratio of the mother liquor volume V_{ml} in the middle chamber of the electrodialysis device and the volumes of the anolyte V_a and the catholyte V_c in the anodic and cathodic chambers respectively, equal to $V_{ml}:V_a = 1:0.5-1.0$ and $V_{ml}:V_c = 1:0.4-0.6$, with obtaining a solution of nitric acid in the anodic chamber, and a solution of sodium and potassium hydroxides in the cathodic chamber. The claimed method allows to obtain crystalline boric acid and highly concentrated solutions of nitric acid and hydroxides of sodium and potassium, suitable for reuse in the NPP process cycle and for general industrial use. Conducting electro-

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dialysis at low values of current and voltage provides a reduction of the method's energy intensity. The involvement of all major components of waste mother liquors

into the processing reduces the amount of stored and disposed hazardous waste.

Description

[0001] The invention is related to integrated recycling of complex liquid boric nuclear waste generated during operation of the nuclear power units, including VVER, and which can be used for extraction of boric and nitric acids, and compounds of alkaline elements to be further re-used in NPP process cycle.

[0002] Among all types of liquid nuclear waste generated by NPPs, evaporator sludge is the most difficult for recycling. This type of waste is high-salt nitrate solution of sodium and potassium, containing borates and hardware corrosion products in the form of transition metals salt, as well as decontamination agents delivered with various effluents. After decontamination the solution is evaporated to be converted into a fusion cake for further storage. This type of waste cannot be 100% recycled.

[0003] There is information about a boron-controlled method of liquid nuclear waste recycling (see patent No 2012076 RF, IPC⁵G21F 9/08, 1994). This method involves vaporization of waste, crystallization of resulting boron-containing concentrate, separation of this concentrate from the mother liquor, dissolution, ultrafiltration of the resulting solution, ion-selective filtration, vaporization up to 80-250 g/l in equivalent of boric acid and crystallization of this acid. The yield of boric acid is less than 84% with impurity content of 10^{-2} - 10^{-3} percent by weight.

[0004] Among the major disadvantages of this method are: high energy consumption for vaporization, low extraction of boric acid, the resulting solutions require post-purification. This method is used for recovery of boric acid only, which means a lot of non-recycled waste for further disposal.

[0005] There is also information about another method selected as a prototype, this is a boron-controlled method of liquid nuclear waste recycling (see patent No 7323613 USA, IPC G21F 9/06, 9/20, G21C 1/00, B01D 61/42 (2006.01), 2008). This method is applied for liquid waste containing sodium and potassium nitrates and includes separate collection of acidic waste ($\text{pH} < 5.5$), which does not contain boric acid, and alkaline waste ($\text{pH} > 5.5$), which contain borates, followed by concentration and mixing, crystallization of sodium borate with pH 8.0-10.1, separation from the mother liquor, treatment of the solution with calcium and magnesium salts, preferable with calcium nitrate or magnesium chloride, and separation of the resulting borate precipitation of calcium or magnesium. Then the sodium borate precipitation is dissolved to reach concentration of 20-25 g/l and expose to electro-dialysis with an electro-dialysis device with anion- and cation-exchange membranes, as a result there are boric acid solutions (0.1-60 g/l) and sodium hydrate solutions (with NaOH content up to 150 g/l). The parameters of electro-dialysis are: current intensity = 0.2-45 A, voltage = 5-55 V

[0006] This method has the following disadvantages: It provides only for the recovery of boric acid and sodium hydrate, while the high-salt mother liquor (which does

not contain borates) is not recycled, which means a lot of non-recycled waste for further disposal. There is another disadvantage of this method: the resulting boric acid solution is un-marketable, and sodium hydrate solution is of low concentration which makes them difficult to re-use. High energy consumption is another disadvantage of this method. The reason is that the sodium borate solution exposed to electro-dialysis has low sodium content and higher electrical resistance, thus higher current intensity and voltage are required for electro-dialysis.

[0007] Purpose of this invention is to achieve a technical result, which can be described as recycling of complex nuclear liquid waste with high salt content to have a broader range of post-recycling products, in particular, marketable boric acid, concentrated solutions of nitric acid, sodium and potassium hydrates, which can be re-used in NPP process cycle. The expected technical result involves achieving lower energy consumption and reduction of the amount of hazardous waste to be buried and to be stored.

[0008] The technical result is achieved through boron-controlled method of recycling liquid nuclear waste which contain sodium and potassium salts, including: adding calcium nitrate to the borate solution with further precipitation of sodium borate and separation of sodium borate from the mother liquor; followed by electro-dialysis using an electro-dialysis device with cation- and anion-exchange chambers; followed by generation of boric acid and sodium and potassium hydrate solutions; in accordance with the invention, the initial borate solution contains sodium and potassium nitrates and sulfates instead of sodium and potassium salts; calcium nitrate is added to the initial borate solution to have calcium borate and sulfate co-precipitated; boric acid is produced by treating calcium borate and sulfate with nitric acid solution with further separation of precipitated calcium sulfate from the calcium borate solution; after that calcium borate solution is treated with nitric acid to cause boric acid precipitation and calcium nitrate solution; boric acid precipitation is separated and dried, and the mother liquor is exposed to electro-dialysis to produce nitric acid solution and sodium and potassium hydrates.

[0009] The technical result is also achieved by adding the calcium nitrate into borate solution with pH 9.3-11.0

[0010] The technical result is also achieved by treating the co-precipitated calcium borate and sulfate with nitric acid solution to reach the value of pH 5-7.

[0011] The technical result is also achieved by treating the calcium borate solution with nitric acid under the temperature of 10-20°C to reach the value of pH 1-3.

[0012] The technical result is also achieved by adding the calcium nitrate solution to the initial borate solution after separation of precipitation.

[0013] The technical result is also achieved by electro-dialysis of the mother liquor in a 3-chamber electro-dialysis device following the pre-defined volume to volume proportion of the mother liquor V_{Mp} in the middle chamber of the electro-dialysis device, and following the volume

proportion of anolyte V_a and catholyte V_k in anode and cathode chambers respectively ($V_{Mp}:V_a=1:0.5-1.0$ and $V_{Mp}:V_k=1:0.4-0.6$), as a result the nitric acid solution will be produced in the anode chamber, while sodium hydrate solution and potassium hydrate solution will be produced in the cathode chamber.

[0014] The technical result is achieved by the following parameters of electrodialysis: current intensity = 1-3 A, voltage = 4-10 V.

[0015] The technical result is achieved by washing the boric acid precipitation with nitric solution (pH 2-3) containing boric acid with content of 30-35 g/l

[0016] The technical result is achieved by drying the boric acid precipitation at a temperature not higher than 60°C.

[0017] The essential features of alleged invention which define the scope of legal protection and are sufficient for achieving the above technical result have the following functions and are relevant for achieving thereof as follows.

[0018] The fact that the initial borate solution contains calcium and sodium nitrates and sulfates means that electrodialysed nitric acid and alkaline solutions are suitable for re-use, after the sulfate ions in the form of slightly soluble products (for example, gypsum, which can be used in construction industry) are removed from the initial solution.

[0019] Adding calcium nitrate into the initial borate solution causes the co-precipitation of calcium borate and sulfate to form, this makes it possible to ensure good extraction of boron compounds from the solution and purify the solution from sulfate ions before electrodialysis.

[0020] Treatment of co-precipitated calcium borate and sulfate with nitric acid solution followed by conversion of calcium borate into the solution and extraction of precipitated calcium sulfate from the calcium borate solution provides for the good separation of boron compounds from the existing impurities and ensures high boron yield in the final product.

[0021] Treatment of calcium borate solution with nitric acid makes it possible to have the boric acid precipitation which can be easily separated from the calcium nitrate solution.

[0022] Drying of washed boric acid precipitation ensures higher boric acid content in the final product.

[0023] Electrodialysis of the mother liquor which is a result of separation of co-precipitated calcium borate and sulfate requires lower current intensity and voltage values, and provides for extraction of usable components in the form of highly concentrated nitric acid solutions, solutions of sodium and potassium hydrates which are suitable for re-use in NPP process cycle.

[0024] The combination of the above features is necessary and sufficient to achieve the technical result of the invention which can be described as having a broader range of resulting products, such as marketable boric acid and concentrated solutions of nitric acid, sodium and potassium hydrates suitable for re-use in NPP process

cycle, as well as reduction of energy consumption and reduction of the amount of hazardous waste to be buried and to be stored.

[0025] For special cases of invention application the following operations and process parameters are preferred:

Adding calcium nitrate to borate solution under pH 9.3-11.0 provides for good extraction of boron compounds from the solution and makes it possible to purify the solution from sulfate ions before electrodialysis. Adding calcium nitrate under pH lower than 9.3 or higher than 11.0 results in partial dissolution of calcium borate followed by lower extraction and co-precipitation.

[0026] The co-precipitation of calcium borate and sulfate should be treated with nitric acid solution to reach pH value of 5-7, because the solubility of borate compounds in this pH range is highest. If the borate solution has pH lower than 5, the boron yield is also lower because slightly soluble boric acid has been formed. This is the reason why it is impossible to produce highly concentrated boron-containing solutions. If the borate solution has pH higher than 7, slightly soluble sodium borates are formed, they make separation of co-precipitation impossible.

[0027] The calcium borate solution should be treated with nitric acid solution to reach pH value of 5-7. Treating the calcium borate solution (pH < 1) with nitric acid will result in excessive consumption of nitric acid for extraction of boric acid precipitation. With pH over 3 the solid yield of boric acid is also lower.

[0028] Treating of calcium borate solution with nitric acid at a temperature of 10-20°C provides for the best conditions for precipitation of boric acid from the solution. If the temperature is above 20°C, the solubility of boric acid increases and the boron yield becomes lower. If treated at a temperature below 10°C, the solution requires to be cooled and the actual yield of the boron does not get higher.

[0029] Adding calcium nitrate solution to initial borate solution after separation of boric acid precipitation makes it possible to reduce the amount of waste and provides for better use of chemical agents.

[0030] If the mother liquor is electrodialysed following the pre-defined volume to volume proportion of the mother liquor in the middle chamber of 3-chamber electrodialysis device, and following the volume proportion of anolyte V_a and catholyte V_k in anode and cathode chambers respectively, it will be possible to control the concentration of resulting products - nitric acid solution, sodium hydrate solution and potassium hydrate solution. If the required intervals ($V_{Mp}:V_a=1:0.5-1.0$ and $V_{Mp}:V_k=1:0.4-0.6$ of the mother liquor volume against the volume of anolyte and catholyte) were not adhered to, it will not be possible to have the nitric acid solutions and alkaline solutions with the necessary concentration range (300 - 600 g/l) for re-use.

[0031] Electrodialysis carried out under the following parameters: current intensity = 1-3 A, voltage = 4-10 V,

ensures over 99% ions to be extracted from the saline solution with lower energy consumption and with the current yield of about 50-70% Electrodialysis carried out under $I < 1\text{ A}$ and $V < 4\text{ V}$ will result in unreasonable increase of the process duration and lower efficiency, with $I > 3\text{ A}$ and $V > 10\text{ V}$ the current yield becomes lower and the energy consumptions rises.

[0032] Washing the boric acid precipitation with nitrate solution ($\text{pH} = 2-3$) with boric acid content of 30-35 g/l provides for removal of impurities to produce the sufficiently pure final product - boric acid (H_3BO_3 .) Boric acid is least soluble in these intervals of process parameters. The boric acid content in the nitrate solution used for washing ensures a stable value of the pre-defined pH values interval for the nitrate solution. Using nitrate solution with boric acid content lower than 30 g/l will cause partial dissolution of the washed precipitation and with the nitrate solution with boric acid content over 35 g/l the washing solution will get precipitated.

[0033] Drying of washed boric acid precipitation under the temperature not exceeding 60°C ensures boric acid mass content in the final product not less than 99.9 percent by weight. If the temperature is above 60°C , the boric acid may turn into an oxide due to deep dehydration. The lower value of temperature interval was defined following the duration of drying process and may be dependent of rarefaction of operational atmosphere.

[0034] The above particular features of the invention will allow to implement this method at its best in terms of the opportunity of have a broader range of products for re-use in NPP process cycle, and to reduce energy consumption and the amount of hazardous waste to be buried and to be stored.

[0035] The core idea of the proposed method can be illustrated with the below Examples.

[0036] Example 1. We take 1,000 ml of initial borate solution which contains, g/l: 104 Na^+ , 50,8 K^+ , 263 NO_3^- , 24 SO_4^{2-} , 5,3 Cl^- , 42 H_3BO_3 , pH (borate solution) = 8,7. pH of initial solution is upgraded to reach the value of 11 by adding 69 ml of NaOH solution (8.5 mole/l) After that 149 ml of $\text{Ca}(\text{NO}_3)_2$ solution (5.5 mole/l) are added to borate solution As a result a co-precipitation of calcium borate and sulfate is generated. After the generated co-precipitation is separated from the solution using the method of filtration, 1,168 ml of mother liquor are electro-dialysed, and co-precipitated calcium borate and sulfate are used for producing boric acid.

[0037] Co-precipitated calcium borate and sulfate are treated with the solution which contains nitric acid (48.4 ml with concentration = 12.2 mole/l) and 120 ml of water to reach the value of $\text{pH} = 5$ with further conversion of calcium borate into a solution and separation of calcium sulfate precipitation (34 g) which, in terms of the equivalent amount of anhydrous salt, is 6.95% of overall salt content in the mother liquor. After that the sodium borate solution is treated with nitric acid solution (48.4 ml, concentration = 12.2 mole/l) at a temperature of 20°C to reach the value of $\text{pH}=1$. The generated boric acid co-

precipitation is separated from calcium nitrate solution, then washed with nitrate solution ($\text{pH}=2$) which contains boric acid (concentration = 35 g/l) and dried at a temperature of 55°C . As a result 32.4 g of boric acid are generated. The calcium nitrate solution is added to the initial borate solution after separation of boric acid precipitation.

[0038] The mother liquor is electro-dialysed in a 3-chamber electro-dialysis device with cation- and anion-exchange membranes. 1,168 ml of mother liquor are exposed to electro-dialysis, the solution contains, g/l: 319 NO_3^- , 0,8 SO_4^{2-} , 4,6 Cl^- , 102 Na^+ , 44 K^+ and 4,8 H_3BO_3 , with $I = 2\text{ A}$, $V = 6\text{ V}$ and following the proportion: $V_{\text{Mp}}:V_{\text{a}}=1:0,5$ and $V_{\text{Mp}}:V_{\text{k}}=1:0,5$ to have as a result 584 ml of nitric acid solution generated in the anode chamber, this solution contains, g/l: 648,3 HNO_3 , 1,63 H_2SO_4 , 9,5 HCl , in cathode chamber there are 584 ml of sodium and potassium hydrate solution, which contains, g/l: 354,8 NaOH , 181,4 KOH , and in the middle chamber there are 1,168 ml of demineralized mother liquor which contains 1,6 g/l of the following ions: NO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ and 4,8 g/l of H_3BO_3 . Ion extraction from the mother liquor is 99.5%. The current yield of electro-dialysed products is 60%.

[0039] Example 2. We take 1,000 ml of initial borate solution which contains, g/l: 111,3 Na^+ , 31,5 K^+ , 244,3 NO_3^- , 35,5 SO_4^{2-} , 10,2 Cl^- , 34,6 H_3BO_3 , solution pH = 8,5. pH of initial solution is upgraded to reach the value of 9,3 by adding 54 ml of NaOH solution (8.5 mole/l) After that 132 ml of $\text{Ca}(\text{NO}_3)_2$ solution (5.5 mole/l) are added to borate solution As a result a co-precipitation of calcium borate and sulfate is generated. After the generated co-precipitation is separated from the solution using the method of filtration, 1150 ml of mother liquor are electro-dialysed, and co-precipitated calcium borate and sulfate are used for producing boric acid.

[0040] Co-precipitated calcium borate and sulfate are treated with the solution which contains nitric acid (41 ml with concentration = 12.2 mole/l) and 150 ml of water to reach the value of $\text{pH} = 7$ with further conversion of calcium borate into a solution and separation of calcium sulfate precipitation (50,3 g) which, in terms of the equivalent amount of anhydrous salt, is 10.8% of overall salt content in the mother liquor. After that the sodium borate solution is treated with nitric acid solution (41 ml, concentration = 12.2 mole/l) at a temperature of 10°C to reach the value of $\text{pH}=3$. The generated boric acid co-precipitation is separated from calcium nitrate solution, then washed with nitrate solution ($\text{pH}=3$) which contains boric acid (concentration = 30 g/l) and dried at a temperature of 60°C . As a result 27.5 g of boric acid are generated. The calcium nitrate solution is added to the initial borate solution after separation of boric acid precipitation.

[0041] The mother liquor is electro-dialysed in a 3-chamber electro-dialysis device with cation- and anion-exchange membranes. 1,150 ml of mother liquor are exposed to electro-dialysis, the solution contains, g/l: 291,4 NO_3^- , 1,2 SO_4^{2-} , 8,9 Cl^- , 106,7 Na^+ , 27,4 K^+ and 3,1 H_3BO_3 , with $I = 2\text{ A}$, $V = 6,2\text{ V}$ and following the proportion:

$V_{Mp}:V_a=1:0,5$ and $V_{Mp}:V_k=1:0,4$ to have as a result 575 ml of nitric acid solution generated in the anode chamber, this solution contains, g/l: 592,2 HNO₃, 2,45 H₂SO₄, 18,3 HCl, in cathode chamber there are 460 ml of sodium and potassium hydrate solution, which contains, g/l: 463,9 NaOH, 56,2 KOH, and in the middle chamber there are 1,150 ml of demineralized mother liquor which contains 1,17 g/l of the following ions: NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, K⁺ and 3,1 g/l of H₃BO₃. Ion extraction from the mother liquor is 99.6%. The current yield of electro dialysed products is 60%.

[0042] Example 3 We take 1,000 ml of initial borate solution which contains, g/l: 101,9 Na⁺, 19 K⁺, 141,1 NO₃⁻, 4,8 SO₄²⁻, 15,1 Cl⁻, 80,3 H₃BO₃, solution pH = 8,2. pH of initial solution is upgraded to reach the value of 10,1 by adding 82 ml of NaOH solution (8.5 mole/l) After that 236 ml of Ca(NO₃)₂ solution (5.5 mole/l) are added to borate solution As a result a co-precipitation of calcium borate and sulfate is generated. After the generated co-precipitation is separated from the solution using the method of filtration, 1,250 ml of mother liquor are electro dialysed, and co-precipitated calcium borate and sulfate are used for producing boric acid.

[0043] Co-precipitated calcium borate and sulfate are treated with the solution which contains nitric acid (103 ml with concentration = 12.2 mole/l) and 200 ml of water to reach the value of pH = 6,6 with further conversion of calcium borate into a solution and separation of calcium sulfate precipitation (6,8 g) which, in terms of the equivalent amount of anhydrous salt, is 1.9% of overall salt content in the mother liquor. After that the sodium borate solution is treated with nitric acid solution (103 ml, concentration = 12.2 mole/l) at a temperature of 18°C to reach the value of pH=2. The generated boric acid co-precipitation is separated from calcium nitrate solution, then washed with nitrate solution (pH =2) which contains boric acid (concentration = 33 g/l) and dried at a temperature of 40°C. As a result 69.3 g of boric acid are generated. The calcium nitrate solution is added to the initial borate solution after separation of boric acid precipitation.

[0044] The mother liquor is electro dialysed in a 3-chamber electro dialysis device with cation- and anion-exchange membranes. 1,250 ml of mother liquor are exposed to electro dialysis, the solution contains, g/l: 241,8 NO₃⁻, 1,4 SO₄²⁻, 12,1 Cl⁻, 94,3 Na⁺, 15,2 K⁺ and 1,9 H₃BO₃, with $I=1\text{ A}$, $V=4\text{ V}$ and following the proportion: $V_{Mp}:V_a=1:0,6$ and $V_{Mp}:V_k=1:0,6$ to have as a result 750 ml of nitric acid solution generated in the anode chamber, this solution contains, g/l: 409,5 HNO₃, 2,38 H₂SO₄, 27,7 HCl, in cathode chamber there are 750 ml of sodium and potassium hydrate solution, which contains, g/l: 273,3 NaOH, 36,4 KOH, and in the middle chamber there are 1,250 ml of demineralized mother liquor which contains 2,42 g/l of the following ions: NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, K⁺ and 1,9 g/l of H₃BO₃. Ion extraction from the mother liquor is 99%. The current yield of electro dialysed products is 70%.

[0045] Example 4 We take 1,000 ml of initial borate

solution which contains, g/l: 155,8 Na⁺, 11,2 K⁺, 227 NO₃⁻, 6 SO₄²⁻, 3,8 Cl⁻, 18 H₃BO₃, solution pH = 12. pH of initial solution is upgraded to reach the value of 10,6 by adding 130 ml of HNO₃ solution (4 mole/l) After that 62 ml of Ca(NO₃)₂ solution (5.5 mole/l) are added to borate solution As a result a co-precipitation of calcium borate and sulfate is generated. After the generated co-precipitation is separated from the solution using the method of filtration, 1,190 ml of mother liquor are electro dialysed, and co-precipitated calcium borate and sulfate are used for producing boric acid.

[0046] Co-precipitated calcium borate and sulfate are treated with the solution which contains nitric acid (23 ml with concentration = 12.2 mole/l) and 150 ml of water to reach the value of pH = 6,2 with further conversion of calcium borate into a solution and separation of calcium sulfate precipitation (8,5 g) which, in terms of the equivalent amount of anhydrous salt, is 2% of overall salt content in the mother liquor. After that the sodium borate solution is treated with nitric acid solution (23 ml, concentration = 12.2 mole/l) at a temperature of 16°C to reach the value of pH=2,3. The generated boric acid co-precipitation is separated from calcium nitrate solution, then washed with nitrate solution (pH =2,3) which contains boric acid (concentration = 33 g/l) and dried at a temperature of 57°C. As a result 15.6 g of boric acid are generated. The calcium nitrate solution is added to the initial borate solution after separation of boric acid precipitation.

[0047] The mother liquor is electro dialysed in a 3-chamber electro dialysis device with cation- and anion-exchange membranes. 1,190 ml of mother liquor are exposed to electro dialysis, the solution contains, g/l: 346 NO₃⁻, 0,8 SO₄²⁻, 3,2 Cl⁻, 130,9 Na⁺, 9,44 K⁺ and 0,6 H₃BO₃, with $I=3\text{ A}$, $V=10\text{ V}$ and following the proportion: $V_{Mp}:V_a=1:1$ and $V_{Mp}:V_k=1:0,5$ to have as a result 1,190 ml of nitric acid solution generated in the anode chamber, this solution contains, g/l: 352 HNO₃, 0,81 H₂SO₄, 3,3 HCl, in cathode chamber there are 595 ml of sodium and potassium hydrate solution, which contains, g/l: 455,3 NaOH, 27,0 KOH, and in the middle chamber there are 1190 ml of demineralized mother liquor which contains 1,04 g/l of the following ions: NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, K⁺ and 0,6 g/l of H₃BO₃. Ion extraction from the mother liquor is 99,7%. The current yield of electro dialysed products is 50%.

[0048] Example 5 We take 1,000 ml of initial borate solution which contains, g/l: 89,2 Na⁺, 22,4 K⁺, 132,7 NO₃⁻, 17,3 SO₄²⁻, 11,7 Cl⁻, 37 H₃BO₃, solution pH = 10,7. After that 336 ml of Ca(NO₃)₂ solution (4 mole/l) are added to borate solution As a result a co-precipitation of calcium borate and sulfate is generated. After the generated co-precipitation is separated from the solution using the method of filtration, 1,220 ml of mother liquor are electro dialysed, and co-precipitated calcium borate and sulfate are used for producing boric acid.

[0049] Co-precipitated calcium borate and sulfate are treated with the solution which contains nitric acid (53 ml

with concentration = 12.2 mole/l) and 150 ml of water to reach the value of pH = 6 with further conversion of calcium borate into a solution and separation of calcium sulfate precipitation (24,5 g) which, in terms of the equivalent amount of anhydrous salt, is 7.9% of overall salt content in the mother liquor. After that the sodium borate solution is treated with nitric acid solution (53 ml, concentration = 12.2 mole/l) at a temperature of 20°C to reach the value of pH=2. The generated boric acid co-precipitation is separated from calcium nitrate solution, then washed with nitrate solution (pH =2) which contains boric acid (concentration = 35 g/l) and dried at a temperature of 60°C. As a result 36.1 g of boric acid are generated. The calcium nitrate solution is added to the initial borate solution after separation of boric acid precipitation.

[0050] The mother liquor is electrodialysed in a 3-chamber electrodialysis device with cation- and anion-exchange membranes. 1,220 ml of mother liquor are exposed to electrodialysis, the solution contains, g/l: 198,4 NO_3^- , 0,9 SO_4^{2-} , 9,6 Cl^- , 79,1 Na^+ , 18,4 K^+ and 2,5 H_3BO_3 , with $I = 1 \text{ A}$, $V = 5 \text{ V}$ and following the proportion: $V_{\text{Mp}}:V_{\text{a}}=1:0,6$ and $V_{\text{Mp}}:V_{\text{c}}=1:0,5$ to have as a result 732 ml of nitric acid solution generated in the anode chamber, this solution contains, g/l: 336 HNO_3 , 1,53 H_2SO_4 , 16,4 HCl , in cathode chamber there are 610 ml of sodium and potassium hydrate solution, which contains, g/l: 275,1 NaOH , 53,1 KOH , and in the middle chamber there are 1220 ml of demineralized mother liquor which contains 1,98 g/l of the following ions: NO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ and 2,5 g/l of H_3BO_3 . Ion extraction from the mother liquor is 99%. The current yield of electrodialysed products is 70%.

[0051] From the above description and Examples 1-5 it is clear that the proposed method of liquid nuclear waste recycling, as compared with the prototype method, allows for production of marketable boric acid (in crystallized form) and highly concentrated solutions of boric acid (up to 648,3 g/l) and sodium hydrate (up to 463,9 g/l) and potassium hydrate (up to 181,4 g/l) which are suitable for re-use in NPP process cycle and for general industrial needs. Electrodialysis carried out at lower values of current intensity and voltage ensures lower energy consumption. The fact that all major components of waste mother liquors are involved in the process of recycling means less hazardous waste to be further buried and stored. Mostly standard chemical equipment is used for this embodiment.

Claims

1. The method of liquid waste processing for NPP with boron control, wherein a waste comprises sodium and potassium salts, including the introduction of calcium nitrate into a borate solution with sedimentation of calcium borate and its separation from the mother liquor, electrodialysis with the use of an electrodialysis device with cation-exchange and anion-ex-

change membranes, obtaining boric acid and sodium and potassium hydroxides solution, wherein the initial borate solution, as sodium and potassium salts, comprises their nitrates and sulphates, they introduce calcium nitrate into the initial borate solution with obtaining a co-precipitation of borate and calcium sulphate, they obtain boric acid through the treating a co-precipitation of borate and calcium sulphate with a solution of nitric acid with separation the calcium sulfate sediment from a solution of calcium borate, after which they treat the solution of calcium borate with nitric acid with formation a sediment of boric acid and a solution of calcium nitrate, they separate and dry the sediment of boric acid and they subject directly mother liquor to electrodialysis with obtaining solutions of nitric acid and sodium and potassium hydroxides.

2. The method according to claim 1, wherein they introduce the calcium nitrate into the borate solution at pH 9.3-11.0.

3. The method according to claim 1, wherein they treat co-precipitation of borate and calcium sulphate with a nitric acid solution until pH 5-7 is provided.

4. The method according to claim 1, wherein they treat calcium borate solution with nitric acid at a temperature of 10-20°C until pH 1-3 is provided.

5. The method according to claim 1, wherein after separation of boric acid sediment they add calcium nitrate solution to the initial borate solution.

6. The method according to claim 1, wherein they conduct mother liquor electrodialysis in a three-chamber electrodialysis device at the ratio of the mother liquor volume V_{ml} in the middle chamber of the electrodialysis device and the volumes of the anolyte V_{a} and the catholyte V_{c} in the anodic and cathodic chambers respectively, equal to $V_{\text{ml}}:V_{\text{a}} = 1:0.5-1.0$ and $V_{\text{ml}}:V_{\text{c}} = 1:0.4-0.6$, with obtaining a solution of nitric acid in the anodic chamber, and a solution of sodium and potassium hydroxides in the cathodic chamber.

7. The method according to claim 1 or 6, wherein they execute electrodialysis at a current value of 1-3 A and a voltage of 4-10 V.

8. The method according to claim 1, wherein they wash the boric acid sediment with a nitrate solution of pH 2-3, comprising 30-35 g/l of boric acid.

9. The method according to claim 1, wherein they dry the boric acid sediment at a temperature not exceeding 60°C.

INTERNATIONAL SEARCH REPORT

International application No.
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5	A. CLASSIFICATION OF SUBJECT MATTER G21F 9/06 (2006.01) G21F 9/20 (2006.01)	
	According to International Patent Classification (IPC) or to both national classification and IPC	
10	B. FIELDS SEARCHED	
	Minimum documentation searched (classification system followed by classification symbols)	
	G21F 9/00, 9/04, 9/06, 9/20	
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)	
	PatSearch, esp@cenet, USPTO, Google	
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT	
	Category*	Citation of document, with indication, where appropriate, of the relevant passages
		Relevant to claim No.
25	A	US 2004/0254417 A1 (VLADIMIROV VLADIMIR ASEN OV) 16.12.2004, the claims
	A	UA 15840 C2 (AKTSIONERNOE OBSHCHESTVO ZAKRYTOGO TIPA "NAUCHNO-PROIZVODSTVENNOE OBEDINENIE") 30.06.1997
30	A	US 4540512 A1 (WESTINGHOUSE ELECTRIC CORP.) 10.09.1985
	A	SU 654010 A (ZHIKHAREV M.I. et al.) 30.12.1979
35		
40	☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.	
45	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
50	Date of the actual completion of the international search 17 August 2018 (17.08.2018)	Date of mailing of the international search report 23 August 2018 (23.08.2018)
	Name and mailing address of the ISA/ RU	Authorized officer
55	Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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